Indian J. Phys. **50**, 975–980 (1976)

On the analysis of phosphorescence decay of hafnium activated strontium sulphide phosphors

S. S. Paliwal and O. P. Sinha*

Department of Physics, Motilal Vigyan Mahavidyalaya, Bhopal

(*Received* 16 *February* 1976, *revised* 2 *June* 1976)

Phosphorescence decay of strontium sulphide phosphors activated with varying amounts of hafnium has been studied at room temperature 305°K The decay curves were analysed by breaking the curves into three exponentials by the method of successive subtraction The phosphorescence decay follows the decay law of the form $I = I_0 t^{-b}$, where the value of decay constant b varies from 0·68 to 0·95. The effective trap levels are found to be distributed from 0·612 to 0·725 eV below the bottom of the conduction band Decay constants as calculated after different times of decay show an increasing tendency with time There is hardly any variation in the trap depth values with the activator concentration, this suggests that the trap distribution is due to the defects produced by the lattice perturbation caused by the incorporation of the activator in the host lattice, and not by the activator itself.

1. Introduction

The problem of determining trap energies is of fundamental importance in the study of luminescence. A possible approach to this problem is the analysis of phosphorescence decay. Decay studies when combined with other experimental data such as those obtained from thermoluminescence or photoconductivity measurements, give useful insight into the type of mechanism involved in the luminescence process This paper reports the results of decay studies of hafnium activated strontium sulphide phosphors

2. Experimental

The phosphors were prepared by heating an intimate mixture of purified strontium sulphate with a suitable flux (sodium sulphate), a reducing agent (A.R. grade carbon), and the requisite amount of activator, for about two hours at a temperature of 930±10°C. Hafnium activator was added in the form of hafnium oxide solution and the concentration was varied from 0·00001 to 0·10 gm in steps

The phosphors were excited to saturation with 3650Å ultra-violet radiation. The after-glow intensity in arbitrary units in terms of galvanometer deflection was measured using a photomultiplier IP21 in conjunction with a multiflex

*S. S. L. Jain College, Vidisha, M.P.

galvanometer. The intensity was recorded from 5 sec after cessation of excitation to a time till it reduced to a very low value.

3 Results

To investigate the nature of decay the logarithm of intensity was plotted against time. Non-linear curves were obtained showing that decay does not follow an exponential law. The logarithm of intensity was plotted against logarithm of time and relation obtained was approximately linear which indicates a hyperbolic decay. To determine the degree of linearity between log t and log I the correlation coefficient (r) was calculated using the formula

$$r = \frac{n\Sigma xy - \Sigma x \Sigma y}{[\{nx^2-(x)^2\}\{n\Sigma y^2-(\Sigma y)^2\}]^{\frac{1}{2}}} \quad \ldots (1)$$

where $x = \log t$, $y = \log I$, and n is the order of observations. The values of r thus calculated for all the phosphors vary from 0·98 to 1·00 indicating a strong linear relationship between log t and log I. The order of observation n in the present case is $n = 15$.

Decay Constant. In the present investigation the decay is found to be of the form

$$I = I_0 t^{-b}, \quad \ldots (2)$$

where b is the decay constant. The values of the decay constant were calculated by the method of least squares for all the samples using the formula

$$b = \frac{\Sigma x \Sigma y - \Sigma xy}{(\Sigma x)^2 - n\Sigma x^2} \quad \ldots (3)$$

The decay constant varies from 0·68 to 0·95.

Variation of Decay Constant with Time

The decay constant after different time periods were calculated by considering only those observations which were taken after t seconds of decay. The representative curves of such variation are shown in Figure 1. These results show that decay constant increases initially with time and then it becomes nearly constant.

Analysis of Decay Curve

Hyperbolic decay can be accounted for by the monomolecular superposition theory. In the investigation of present phosphor system, the decay curves were analysed into three exponentials by the method of successive subtraction (Bube 1954) shown in Fig. 2. Trap depths corresponding to these exponentials were calculated from the slope of the straight lines on the semi-logarithm plot.

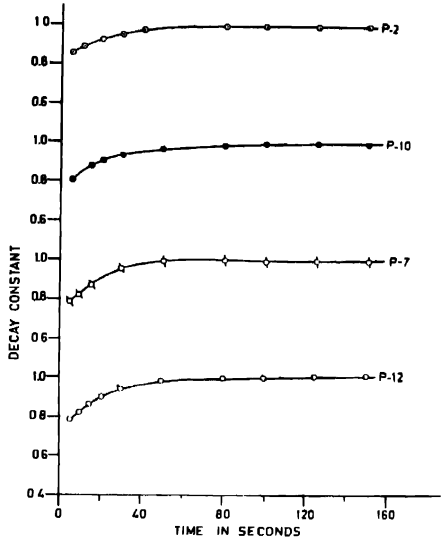

Fig. 1. Decay constant as a function of time.

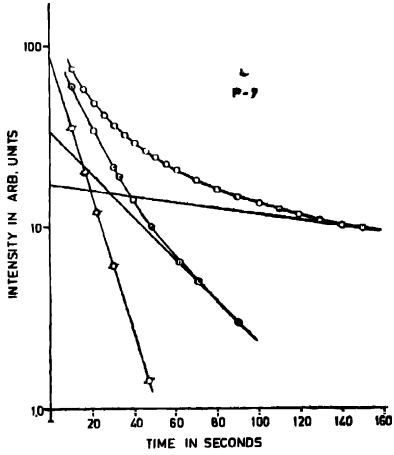

Fig. 2 *Peeling off* of decay curve.

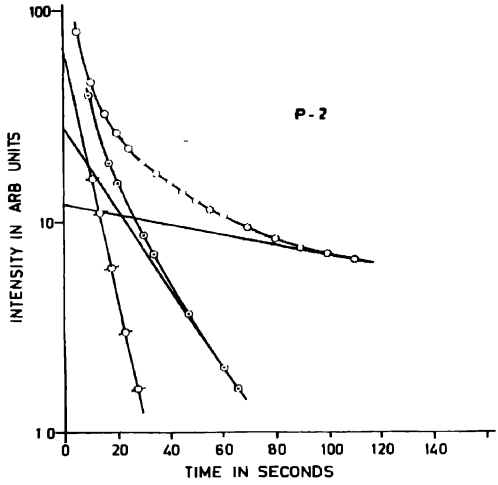

Fig. 2(a). *Peeling off* of decay curve.

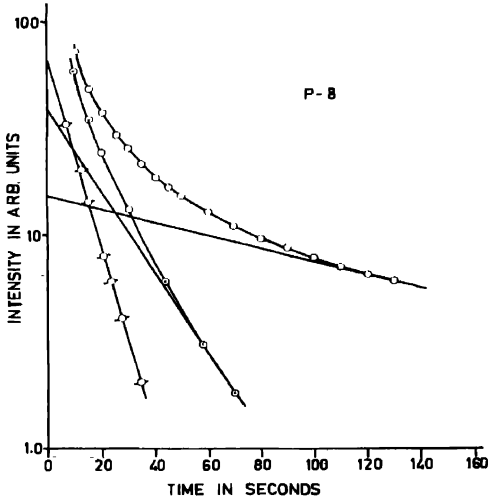

Fig. 2(b). *Peeling off* of decay curve.

According to Randall & Wilins (1945), if all the traps have the same depth E, the probability of escape of an electron from a trap is given by

$$p = S \exp\left(-\frac{E}{kT}\right), \qquad \ldots \quad (4)$$

where S is the frequency factor, k is the Boltzmann constant, and T is the absolute temperature. This equation neglects the effect of retrapping of electrons and non-radiative transitions and assumes that S and E are independent of temperature. For single trap level, the intensity will decay as

$$I = I_0 \exp(-pt), \qquad \ldots \quad (5)$$

where I_0 is the intensity at time $t = 0$ and I is the intensity at a time t after the cessation of excitation.

From eqs (4) and (5), the expression for E becomes

$$E = kT\left[\log_e S - \log_e\left\{\frac{\log_e (I_0/I)}{t}\right\}\right] \qquad \ldots \quad (6)$$

The values of trap depth were calculated for the three exponentials using eq. (6) and taking $S = 2{\cdot}847 \times 10^9$ per sec as obtained from thermoluminescence study. The trap depth varies from 0·612 to 0·639 eV, 0·651 to 0·672 eV and 0·701 to 0·725 eV for the fastest, middle and slowest exponentials respectively.

4 Discussion

The hyperbolic nature of decay curve can easily be explained by assuming the monomolecular kinetics and by *peeling off* the curve into three exponentials. The deviation of decay constant from unity excludes the possibility of uniform distribution of traps. It may be taken as quasi-uniform. The increase of decay constant with time may be considered as due to the presence of traps of different depths. In the initial stages, shallower traps are effective and the decay is rapid, whereas during the latter stages of decay deeper traps are effective and the decay is slow. The variation of decay constant with activator concentration may be due to the non-radiative transitions due to concentration quenching. Further it is also not possible to keep the size of gram the same, which also affects the results as observed by various workers.

The values of trap depth show practically no variation with the activator concentration. This suggests that trap distribution may be due to the defects produced by the lattice perturbation caused by the incorporation of the activator in the host lattice or a native defect of the host lattice, and not due to the activator itself. Similar observations have been made by earlier workers on alkaline earth sulphide phosphors doped with different activators (Sharma & Singh 1969;

Pawar & Narlikar 1973; Jain & Ranade 1974). In all these phosphors, irrespective of the flux or the activator used a trap depth of approximately the same magnitude is obtained under identical experimental conditions (Sivaraman & Bhawalkar 1971; Jain & Sinha 1974). Curie (1968) has reported that the trap group corresponding to about 0·68 is independent of the activator concentration. Thus it appears that this particular group of trap is characteristics of the host lattice itself.

Table 1. Decay constant, correlation coefficient, trap depth as calculated from decay curves

Sample No.	Amount of activator added in gm.	Decay constant	Correlation coefficient	Trap depth in eV due to exponential		
				Slow-I	Medium	Fast
P- 1	0.10	0.762	0 99	0.701	0.645	0.619
P- 2	0.08	0 815	1.00	0.706	0.651	0.625
P- 3	0 06	0.819	0.99	0 710	0.663	0 635
P- 4	0.05	0 835	1 00	0.725	0 672	0 639
P- 5	0 03	0 805	1 00	0 718	0.669	0 646
P- 6	0.01	0.807	1.00	0.717	0 667	0 637
P- 7	0.008	0 789	0 98	0 720	0 657	0 637
P- 8	0.006	0 915	1.00	0.703	0 660	0.632
P- 9	0.003	0 797	0 99	0.706	0 657	0 620
P-10	0 001	0 804	1 00	0 710	0.664	0 631
P-11	0 0008	0 805	1 01	0 705	0.650	0.612
P-12	0 0006	0.791	1.00	0 709	0 667	0 638
P-13	0 0003	0 782	1 00	0.712	0.659	0 629
P-14	0.00001	0 743	1 00	0.706	0 654	0 618
P-15	0.00008	0 740	0 99	0.709	0.654	0.621
P-16	0.00006	0.709	1 00	0.715	0.666	0.634
P-17	0.00003	0.686	1.00	0.713	0 652	0.616
P-18	0.00001	0 692	0.99	0.709	0.650	0.620

References

Bube R H 1950 *Phys. Rev* **80**, 655

Curie D 1963 *Luminescence in Crystals*, Methuen & Co., London, p. 156

Jain K. L. & Ranade J D 1974 *Indian J. Physics* **48**, 353.

Jain S K & Sinha O P 1974 *Indian J Phys* **48**, 1080

Pawar S L & Narlikar A V 1973 *Ind. J Pure & Appl Phys.* **11**, 892

Randall J T & Wilkins M H F 1945 *Proc. Roy. Soc* **A184**, 366.

Sharma D & Singh A 1969 *Indian J Pure & Appl Physd.* **7**. 310.

Sivaraman S. & Bhawalkar D. R 1971 *Ind J Pure & Appl Phys.* **9**, 18.